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EPITAXIAL GROWTH AND STUCTURE OF CUBIC AND PSEUDOCUBIC PEROVSKITE FILMS ON PEROVSKITE STUSBTRATES

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EPITAXIAL GROWTH AND STRUCTURE OF CUBIC AND PSEUDOCUBIC PEROVSKITE FILMS ON PEROVSKITE SUBSTRATES

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ABSTRACT

Cubic and pseudocubic perovskite films on perovskite substrates are used to study the influence of the lattice mismatch on the epitaxial growth of thin films on substrates of the same structure. For the growth of the films, a metalorganic deposition route (MOD) using 2-ethylhexanoates and neodecanoates as precursors, was developed. The decomposition of the precursors was investigated with thermogravimetric analysis (TGA) and x-ray diffraction (XRD). The films were spin-coated on (001)-oriented $SrTiO_3$- and $LaAlO_3$-substrates, pyrolyzed and afterwards annealed between 600°C and 1200°C. XRD-investigations and conventional transmission electron microscopy (CTEM) show, that epitaxial films with the orientation relationship [100](001) film ‖ [100](001) substrate can be grown. With XRD, it could be shown, that not only ternary oxide films ($SrZrO_3$, $BaZrO_3$ and $BaCeO_3$), but also perovskite solid soulution films ($SrTi_{0.5}Zr_{0.5}O_3$ and $BaCe_{0.5}Zr_{0.5}O_3$) can be prepared. Strong interdiffusion, detected by a shift of the film lattice parameter towards the substrate lattice parameter was found in $SrZrO_3$- and $BaZrO_3$-films on $SrTiO_3$, annealed at temperatures above 1050°C. High resolution electron microscopy (HREM) studies of $SrZrO_3$ on $SrTiO_3$ show that a crystalline semicoherent interface with a periodical array of misfit dislocations is present.

INTRODUCTION

The aim of the study is to investigate the epitaxial growth and structure of thin films on substrates of the same structure in dependence of the lattice mismatch. The model system used in this work are thin films of cubic and pseudocubic perovskites ($SrZrO_3$, $BaZrO_3$ and $BaCeO_3$) and solid solutions ($SrTi_{0.5}Zr_{0.5}O_3$ and $BaCe_{0.5}Zr_{0.5}O_3$) on perovskite substrates ($SrTiO_3$ and $LaAlO_3$).

For the processing of the films, metalorganic deposition (MOD) was applied [1,2]. The substrates are spin-coated with metalorganic precursors that decompose during heating into the desired inorganic product (pyrolysis). An annealing at high temperatures promotes grain growth and under certain conditions initiates epitaxial growth [3]. This method provides a way to prepare films with a relatively cheap equipment. Solid solution films, prepared by mixing together different precursors in the appropriate stoichiometry prior to spin-coating, can also be grown, allowing a continuous variation of the film lattice parameter.

To the knowledge of the authors, none of these systems have been prepared by MOD. Due to its lattice constant close to MgO, $BaZrO_3$ can substitute for MgO as a substrate material. Epitaxial films of $BaZrO_3$ on $SrTiO_3$, grown by sputtering were investigated by Y. Dansheng et al. [4]. A.E.M. De Veirman used $BaZrO_3$ on $SrTiO_3$ as substrate for $PbTiO_3$-films [5,6].

$SrTiO_3$ and $BaZrO_3$ are cubic at room temperature (space group Pm3m), whereas the other systems are just cubic in a high temperature phase [7]. In the current study, the epitaxial growth occurs at high temperatures where both the film and substrates have a cubic structure. During cooling, phase transformations can occur in specific systems. The lattice constants of $BaCeO_3$, $BaZrO_3$, $LaAlO_3$, $SrZrO_3$ and $SrTiO_3$ at room temperature are listed in the JCPDS-file [8]. As the deviations from cubic symmetry are small ($<< 1\%$), the orthorhombic lattice constants of

$SrZrO_3$ and $BaCeO_3$ and the hexagonal ones of $LaAlO_3$ have been transformed to pseudocubic notation. The lattice constants of the solid solutions, that have an unknown structure, have been estimated by using Vegard's law. The average lattice constants in pseudocubic notation and the lattice mismatches for the systems investigated, are listed in Table I. As the table shows, the lattice mismatch can be chosen to be as large as 16%.

Table I: Cubic and pseudocubic lattice constants a (nm) and mismatches $\varepsilon(\%)$ at room temperature referred to the substrates $SrTiO_3$ (a=3.905Å) and $LaAlO_3$* (a=3.79Å).

	a (nm)	$\varepsilon_{STO}(\%)=\frac{a-a_{STO}}{a_{STO}}$	$\varepsilon_{LAO}(\%)=\frac{a-a_{LAO}}{a_{LAO}}$
$SrTi_{0.5}Zr_{0.5}O_3$ **	≈ 0.4003	≈ 2.5	***
$SrZrO_3$*	≈ 0.4101	≈ 5.0	≈ 8.2
$BaZrO_3$	0.4193	7.4	≈ 10.6
$BaCe_{0.5}Zr_{0.5}O_3$ **	≈ 0.4296	≈ 10.0	***
$BaCeO_3$ *	≈ 0.4398	≈ 12.6	≈ 16.0

* pseudocubic
** symmetry unknown, lattice constants calculated with Vegard's law
*** not investigated

EXPERIMENT

Thin films of $SrZrO_3$, $BaZrO_3$, $BaCeO_3$ and solid solutions ($SrTi_{0.5}Zr_{0.5}O_3$ and $BaCe_{0.5}Zr_{0.5}O_3$) were prepared by spin-coating (001)-oriented, polished $SrTiO_3$- and $LaAlO_3$-substrates with metalorganic precursors. Before spin-coating, the substrates were cleaned with three different solvents (TCE, acetone and iso-propanol) and heated for 2h at 1400°C to remove plastic deformation produced by polishing. Stoichiometric mixtures of Ce- and Zr-2-ethylhexanoates, Ba- and Sr-neodecanoates and Ti-2-ethylhexoxide were used (STREM Chemicals, Newburyport, MA, USA). These metalorganic precursors were dissolved in toluene, such that the molarity of the final precursor-solution was about 0.25M. The solutions were stirred for at least 15 minutes to ensure good mixing of the cations at the molecular level. Homogeneous films can only be obtained when the precursors are completely dissolved. Precipitates in the precursor-solution lead to inhomogenous coatings and therefore inhomogeneous films. In some cases, especially for solutions containing the Ba-neodecanoate-precursor, it was necessary to filter the precursor-solution (filter:0.2µm) in order to remove precipitates.

The decomposition of the precursor-solution into the perovskite material during heat treatment was investigated by thermogravimetric analysis (TGA) and x-ray powder diffraction using silicon as an internal standard.

Two drops of precursor-solution were put in the middle of the substrate with a pipette. After each drop, the substrate was spun for 10s with 4000rpm. In order to pyrolyze the precursor and initiate epitaxial growth, the films were heated up to temperatures between 600°C and 1200°C (heating rate: 10°C/min, annealing time: 1h). The characterization of morphology and structure was done by x-ray-diffraction (XDS2000, Scintag Inc., Sunnyvale, CA, USA and MRD, Philips Eindhoven, The Netherlands) and scanning electron microscopy (SEM, JEOL 6300FE). For conventional transmission electron microscopy (CTEM) a JEOL2000FX operated at 200kV and for high resolution microscopy (HREM) a JEOL4000EX operated at 400kV were used. The TEM sample preparation is described elsewhere [9].

RESULTS

Precursor Characterization

Thermogravimetric analysis (TGA) of $SrZrO_3$-, $BaZrO_3$- and $BaCeO_3$-precursor solutions were done in air with a heating rate of 10°C/min. All precursors lost most of their weight at temperatures lower than 400°C. Fig. 1 shows the TGA of the $SrZrO_3$-precursor. The high weight loss during heating is due to the evaporation of solvent and the pyrolysis of the metalorganic precursor into inorganic powder. During cooling, the weight was almost constant. X-ray diffraction showed that precursors annealed at 1000°C and cooled down to room temperature have the perovskite phase with lattice constants that agree with literature values (Table II). For the determination of the lattice constants, silicon was added as an internal standard.

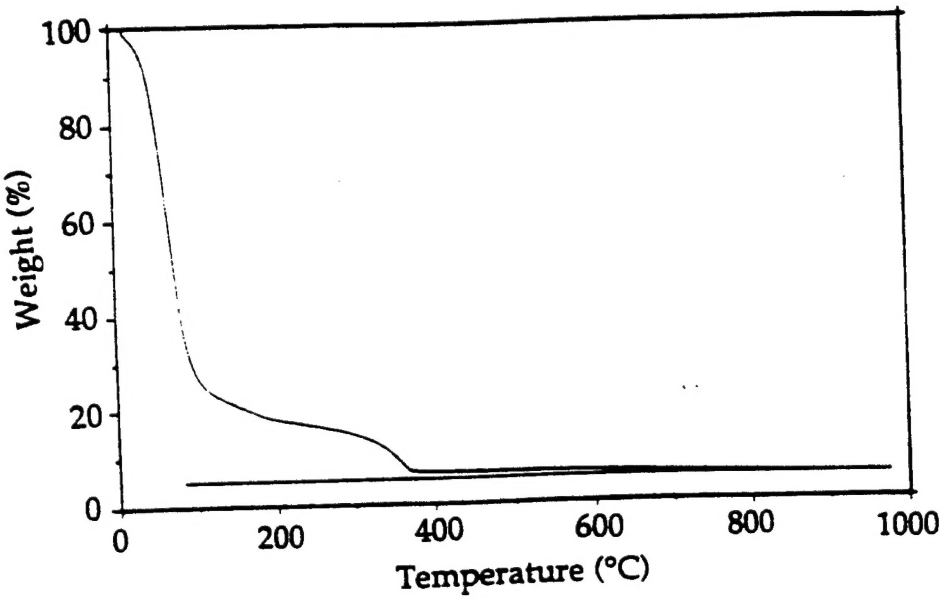

Fig. 1 TGA of a $SrZrO_3$-precursor shows the high weight loss during the evaporation of solvent (T<100°C) and pyrolysis (T<400°C).

Table II: The lattice constants a (nm) of annealed precursor powder, determined by XRD agree well with values from the literature a_{Lit} (nm) .

Precursor	a (nm)	a_{Lit} (nm)
$SrZrO_3$	0.4099 ± 0.0006	≈ 0.4101
$BaZrO_3$	0.4187 ± 0.0006	0.4193
$BaCeO_3$	0.4394 ± 0.0006	≈ 0.4398

Thin films

XRD-investigations demonstrated, that in all systems annealed at temperatures lower or equal than 1000°C (1h) [100](001) film ∥ [100](001) substrate was the only or the dominant orientation relationship between film and substrate. For systems with a large mismatch ($BaCeO_3$ on $SrTiO_3$ and $LaAlO_3$) also little amounts of (110)-orientation and other phases were observed.

It is known from literature, that solid solutions between perovskites, for example between $SrTiO_3$ and $SrZrO_3$ can be formed [10]. XRD-investigations of solid solution thin films of $SrTi_{0.5}Zr_{0.5}O_3$ and $BaCe_{0.5}Zr_{0.5}O_3$ on $SrTiO_3$ confirm, that no phase separation into single

phase perovskites occurs. The films were annealed at 1000°C ($SrTi_{0.5}Zr_{0.5}O_3$) and 800°C ($BaCe_{0.5}Zr_{0.5}O_3$) for 1h. In Fig. 2, XRD-spectra of the solid solution films are presented.

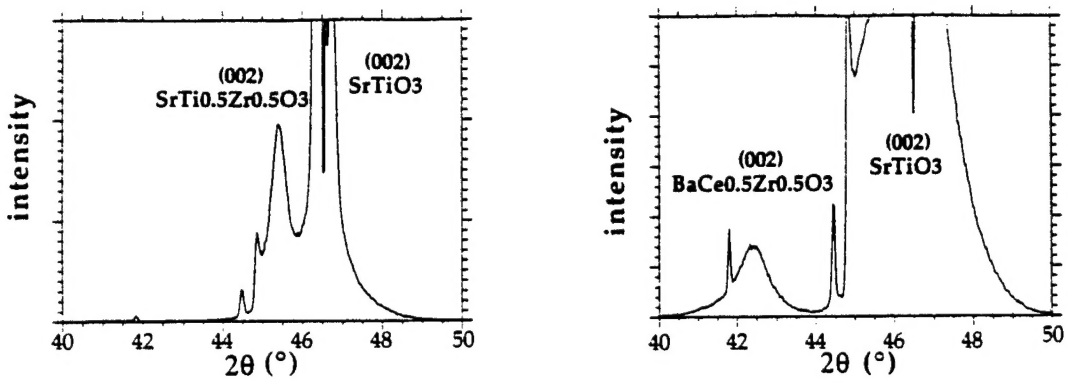

Fig. 2 XRD of a) $SrTi_{0.5}Zr_{0.5}O_3$- and b) $BaCe_{0.5}Zr_{0.5}O_3$-films on $SrTiO_3$. The position of the (002)film x-ray-peaks proves that solid solution films with the out-of-plane orientation (001)film ‖ (001)$SrTiO_3$ can be grown.

XRD-polefigures indicate that the in-plane orientation of these films is [100]film ‖[100] $SrTiO_3$. In Fig. 3 the (002)- and (110)-polefigures of $BaCe_{0.5}Zr_{0.5}O_3$ and the (110)-polefigure of $SrTiO_3$ are shown.

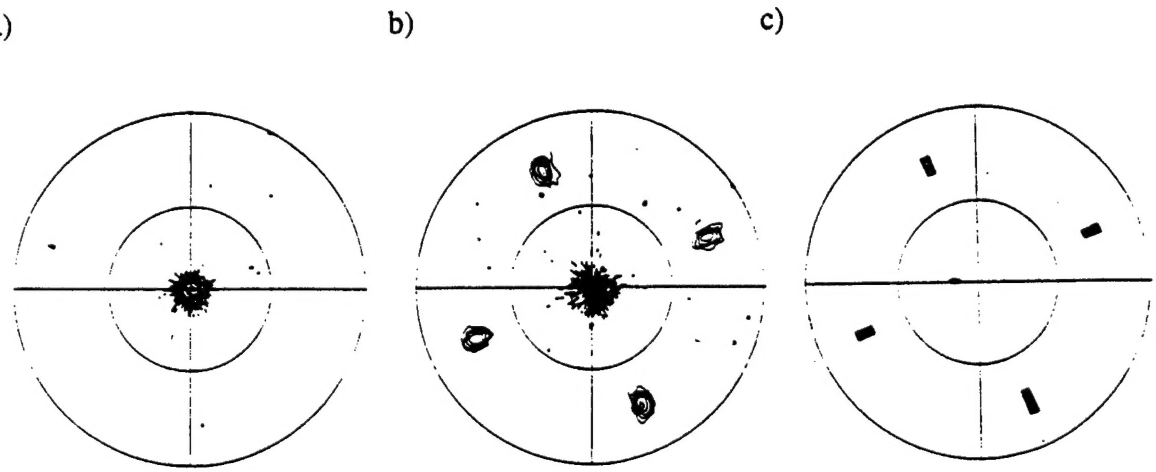

Fig. 3 XRD-polefigures of a) (002)- and b) (110)$BaCe_{0.5}Zr_{0.5}O_3$ and c) (110)$SrTiO_3$ demonstrate the in-plane orientation relationship [100] film ‖ [100] substrate between the solid-solution film and the substrate.

XRD-investigations of $SrZrO_3$- and $BaZrO_3$-films on $SrTiO_3$ annealed above ≈1050°C show a significant shift of the (002) film peak towards the (002) substrate peak, indicating that interdiffusion takes place. That is, solid solution thin films not only can be obtained by mixing different precursors prior to spin-coating, but also by interdiffusion at sufficient high annealing temperatures.

Selected area diffraction (SAD) at TEM-cross-section samples of $SrZrO_3$ on $SrTiO_3$ confirms that epitaxial films with the orientation relationship [100](001) $SrZrO_3$ ‖ [100](001) $SrTiO_3$ have been grown (Fig. 4). The thickness of the film is about 45nm.

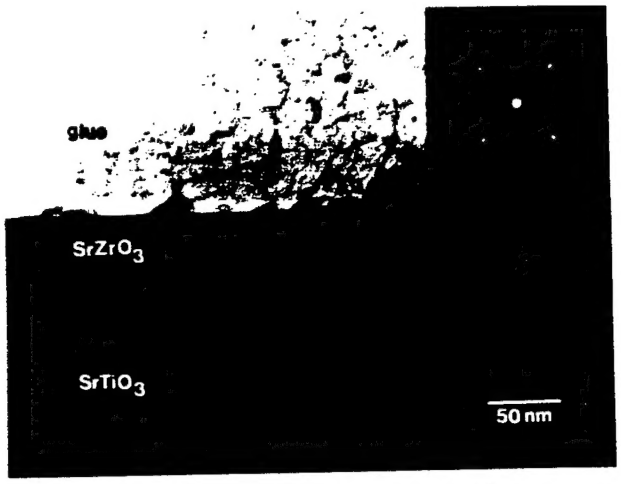

Fig. 4 CTEM-micrograph of a cross-section sample of $SrZrO_3$ on $SrTiO_3$, annealed at 900°C (1h). SAD shows the epitaxial orientation of the film.

Results obtained with high resolution electron micrscopy (HREM) indicate that a semicoherent interface with periodically ordered dislocations in the substrate is present (Fig. 5). A preliminary interpretation suggests, that the misfit dislocations are located in a quadratic arrangement with Burgers-vectors of [100]-type.

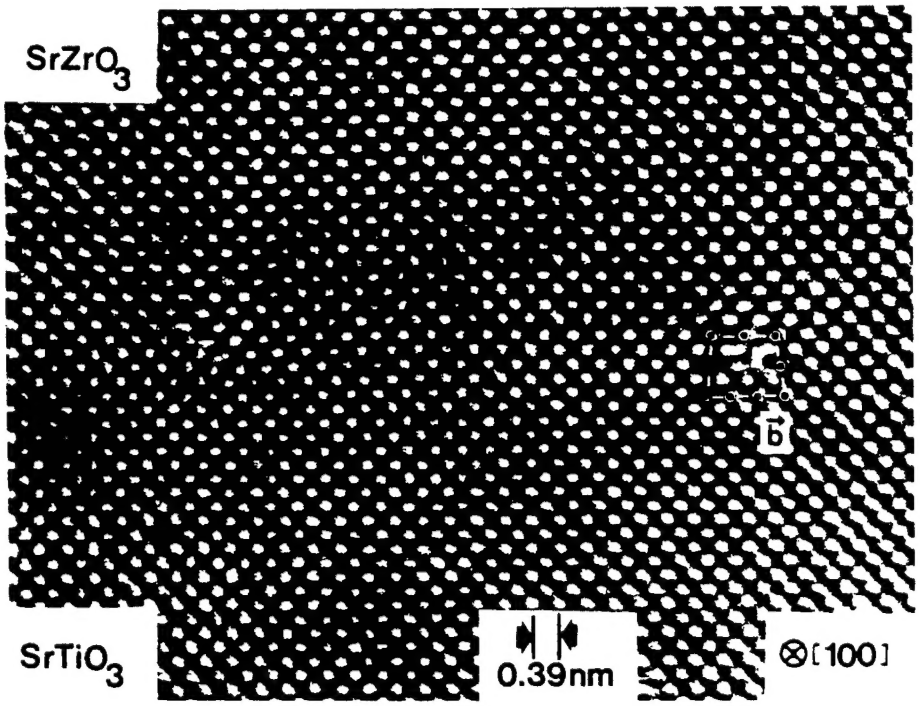

Fig. 5 HREM-image of $SrZrO_3$ on $SrTiO_3$ (900°C/1h) in <100> zone-axis shows periodically ordered dislocations.

CONCLUSION

The investigation of the structure of the interface and the role of interdiffusion in the epitaxial growth is a subject of current research and will be detailed in the future. Our current HREM-results of $SrZrO_3$ on $SrTiO_3$ show, that a crystalline semicoherent interface with misfit dislocations is obtained.

The results underline, that MOD can be used to produce high quality epitaxial films. However, due to the large shrinkage of the precursor material, the method is restricted to very thin films (< 1μm).

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